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ELIMINATION OF SAMPLE CHARGING IN UV PHOTOEMISSION FROM SINGLE CRYSTALS OF SEVERAL POLYCYCLIC HYDROCARBONS

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UV photoemission spectra of single crystals of polycyclic hydrocarbons were measured using two methods, 1) covering a sample with a thin layer of gold and 2) inducing photoconduction in the sample with low-energy light, to eliminate sample charging. Their ionization thresholds obtained are all smaller than the values for corresponding polycrystalline thin films.

Electrons emitted from the surface of a solid insulator leave net positive charges behind. This sample charging smears out the features in its photoemission spectra.[1,2] An example of drastic charging effect on the spectra is shown in Fig. 1 (Curve *a*). Most studies on photoemission from organic solids, which are mostly insulators, have been carried out with thin (a few tens of nm) polycrystalline films evaporated onto a metal substrate.[3] Those films were thin enough for charge carriers to be effectively transported between the conducting substrate and the specimen surface.

In this letter, we describe two methods successfully used to overcome the sample charging; 1) covering a sample with a thin overlayer of gold and 2) inducing photoconduction in the sample with illumination of low-energy light.[2,4] We also report photoelectron spectra and ionization thresholds of single crystals of several polycyclic hydrocarbons obtained from the measurements applying the above methods.

Details of the equipment used for photoemission measurement were already

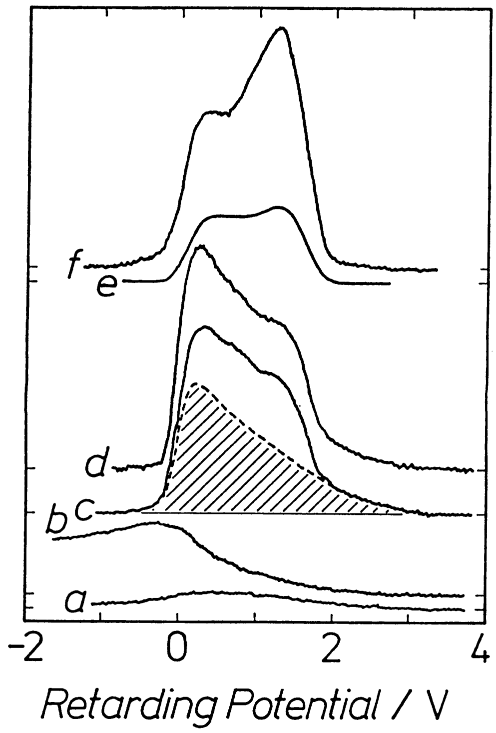

Fig. 1. Photoelectron spectra of an anthracene single crystal. (Exciting photon energy is 7.75 eV.) The abscissa is the retarding potential. *a*, with a 2.3 nm-thick gold overlayer; *b*, *a* illuminated by a tungsten lamp; *c*, *a* with an additional 1.7 nm-thick layer and the estimated contribution of the electron emission from gold is indicated; *d*, *c* with the subsidiary illumination; *e*, obtained from *c* by subtracting the contribution of gold; *f*, measured for a very thin crystal only with the subsidiary illumination.

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described elsewhere.5,6) Essentially photoelectron spectra were obtained by differentiating the current yield for a given incident photon energy as a function of retarding potential applied between a sample and a surrounding collector sphere.

A flat crystal was so mounted that its normal was at 45° with the incident UV light beam. The crystal was simultaneously illuminated with a second lamp, when necessary, that was at right angle with the source. A tungsten lamp or a mercury lamp was used as the second source. The latter supplied high intensity light in the energy range from $\approx$ 2 to 4 eV where the photoconduction was induced. The light out of this energy range was cut off with an optical filter.

Sample crystals of 10 - 40 mm^2 in size and several tens of μm to 1 mm in thickness were used. They were grown in a plate sublimator7) applied a large temperature-gradient to obtain a flat and thin specimen. Scintillation grade of anthracene purified with zone-refining was used. The impurity content of pyrene crystals used in this work was less than 10^{-5} mol/mol. Perylene and benzo[*ghi*]perylene were purified by repeated temperature-gradient sublimation. The crystals developed their faces along the *ab* planes.

A gold layer for overlayer-method was deposited onto the sample surface by fast evaporation from a tungsten boat in a vacuum chamber. Its thickness was measured with a quartz oscillator. The specimen was attached to a sample holder with silver paste, and electrical contact between the sample holder and the gold layer was also made with silver paste painted beforehand on the sides of the crystal, because little or no gold is deposited there due to the arrangement of the crucible in the chamber.

The overlayer-method was first applied to the measurement of photoemission from solids as described hereafter. As photoexcited electrons can escape only from near-surface of the solid, the conductive overlayer must be thin enough to let those electrons pass through with no interference. The escape depth for slow electrons (less than 5 eV above the vacuum level in gold) is 2 - 4 nm.8) Gold layers of such thickness, however, are inhomogeneous, which are characteristic of segregated island structure.9) Thus the thickness monitored is merely averaged value. The size of such an island ranges 10 - 10^3 nm, and it depends on depositing condition and surface nature of the crystal.

A thin gold layer deposited on an anthracene crystal through slow evaporation ($\ll$ 0.1 nm/s) could not reduce the charging effectively. But a layer thicker than 1.5 nm evaporated in rather fast rate (> 0.5 nm/s) with a tungsten boat at a distance of a few cm from the crystal could almost eliminate the surface charging effect on the spectra. In the layer thus obtained oblong chunks (< 5 μm in size) were observed with an electron microscope. They were partly interconnected and formed a conducting network on the surface of the crystal. A layer prepared in slow evaporation may not form such a conducting network that spreads enough to contribute to the surface conduction. Layers thicker than 4 nm affected the spectra seriously in intensity and lineshape. The layer thickness, however, was not the only factor that dominated quality of the spectra.

The spectra of an anthracene crystal shown in Fig. 2 were obtained with a gold layer of only 1.5 nm thickness. On the other hand, as shown in Fig. 1, a spectrum with a 2.3 nm-thick layer was totally deformed due to the charging (Curve *a*), whereas further deposition of a 1.7 (total 4.0)nm-thick layer caused almost complete disappearance of the surface charging (Curve *c*). A clear spectral change from charged to uncharged generally occurred for a layer deposited by a step thicker than 1 nm. When we tried to find the optimal thickness of the layer with successive deposition by thinner steps, the spectra changed from charged to uncharged indeed more gradually, however, all the spectra showed intensities lower than those for a film with the layer of > 1 nm deposition and were affected by electron-scattering. This might be due to a different structure of the overlayer built up in this way.

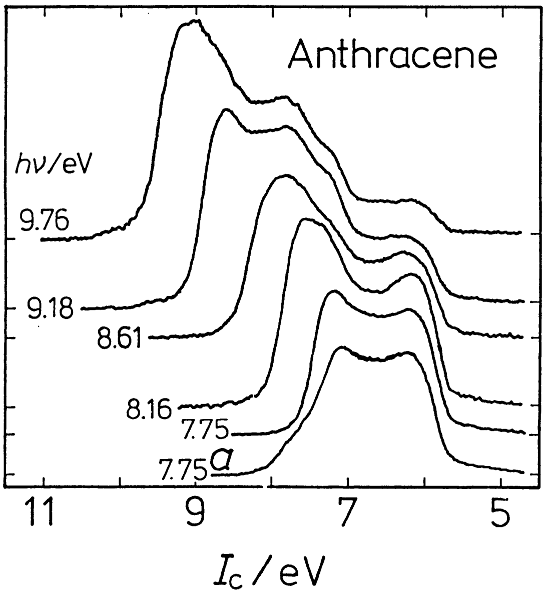

Fig. 2. Photoelectron spectra of an anthracene single crystal obtained using both the overlayer-method and the subsidiary illumination. The abscissa is the ionization energy in the solid state. The thickness of a gold overlayer is 1.5 nm. Curve *a* measured without the illumination still shows the sample charging.

Sample charging on a flat crystal thinner than 0.1 mm could be eliminated by only illuminating with a second lamp. In many cases of measurements using the overlayer-method some remaining charging could also be reduced by the subsidiary illumination. The illumination enhances photoconduction near the crystal surface, and contributes to a better electrical contact among poorly interconnected sections in the layer and probably also between the surface layer and crystal sites in the bulk. The examples are illustrated in Figs. 1 and 2. Using the overlayer-method, the photoinduced current can be transmitted to the substrate not through the crystal but in the surface layer. Thus, the thickness of the crystal is of no importance to the measurement.

Electrons emitted from a gold layer itself may contribute to the spectra. Subtracting this contribution estimated from the gold spectrum gives a spectrum of an anthracene crystal without overlayer (see Curves *e* and *f* in Fig. 1). This shows that there is no noteworthy interaction between the overlayer and the surface of the crystal. No difference was found in the ionization thresholds for the crystal with and without the layer. It is also convenient for this method that gold has a low quantum yield of photoemission for the photon energy range involved in this work.10) Thus, it is one condition for applicability of the overlayer-method to photoemission spectroscopy that the quantum yield of the sample is high enough to enable us to distinguish the contribution of electrons emitted from the sample in the spectra.

Table 1 lists the ionization thresholds of the crystals studied in this work.

Table 1. Ionization thresholds of polycyclic hydrocarbons in the single crystalline and polycrystalline states, I_c^{th} and I_s^{th}, respectively.

Compound	I_c^{th}/eV	I_s^{th}/eV	ΔI^{th}/eV
Anthracene	5.67	5.75 11)	0.08
Pyrene	5.58	5.8 12)	0.22
Perylene	5.12	5.2 13)	0.08
Benzo[*ghi*]perylene	5.26	5.4 3)	0.14

They are compared with those measured for polycrystalline thin films. This shows that the ionization threshold for a single crystal is slightly smaller than that for its thin film, although smaller values in the differences are comparable to the resolution of the electron energy analyzer. The large discrepancy noted for pyrene may be due to low crystallinity in the film, which was estimated by the smeared spectra,[12] since the spectra obtained with the single crystal are rich in features as shown in Fig. 3. Therefore, the value 5.58 eV should be more reliable for the ionization threshold of pyrene in the crystalline state. In the other cases, spectral features for the thin films are almost the same as those for corresponding crystals.

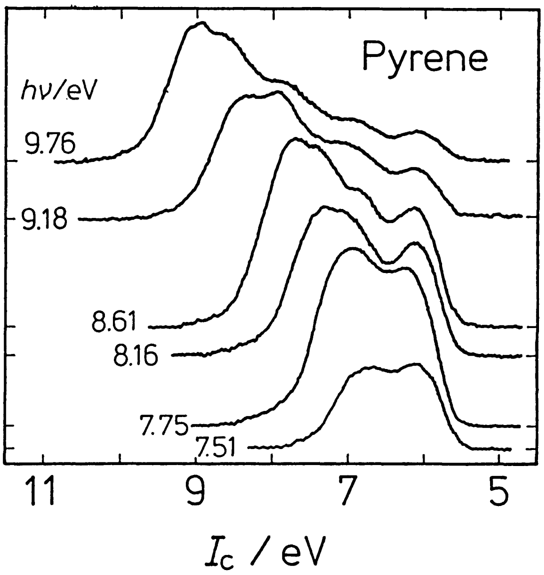

Fig. 3. Photoelectron spectra of a very thin single crystal of pyrene obtained using only the subsidiary illumination.

One possible explanation for the finding of the smaller ionization threshold for single crystals is that an evaporated film has a total crystal surface area per unit sample area illuminated by vacuum UV larger than that of a single crystal due to its polycrystalline structure. Molecules at the surface have an ionization energy larger than those of deeper-lying molecules,[14] since the polarization energy[3] on the surface is smaller than that in the bulk.

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